Super-periodicity in $(1-x)(ZrO_2)–x(Y_2O_3)$ [x = 0.11; 0.40] and its Relationship to Electrical Conductivity

Alicia Brune and David J. Smith
Center for Solid State Science
Arizona State University
Tempe, AZ 85287-1704

The microstructure of $(1-x)(ZrO_2)–x(Y_2O_3)$ [x = 0.11; 0.40] was studied by High Resolution Transmission Electron Microscopy (HRTEM). The purpose of this work was to investigate super-structures due to long range ordering of point defects and to relate their presence to changes in electrical conductivity. The material was prepared by precipitation from inorganic aqueous solutions [1]. Samples (S) with 11 mol.% Y_2O_3 were annealed at three temperatures (S1: 600 C, 1 hour; S2: 1450 C, 2 hours; S3: 1700 C, 3 hours). S4, with 40 mol.% Y_2O_3, was annealed as reported to obtain an ordered, rhombohedral phase $Zr_3Y_4O_{12}$ [2]. Crystalline phases, determined by powder XRD, were S1: cubic/tetragonal; S2 and S3: cubic; S4: reported rhombohedral [2]. In the HRTEM study, selected area electron diffraction patterns (SAED) and electron micrographs were taken at 400KV, with a JEOL 4000 TEM. Digital diffraction patterns (DDP) were obtained from regions in the micrographs.

HRTEM micrographs showed that S1 consisted of agglomerates of nano-sized crystallites with cubic/tetragonal structure; long range ordering of defects was not observed. S2 consisted of larger crystalline grains, with dominant fluorite phase and domains with super-periodicity (Fig. 1); corresponding lattice spacings were obtained from DDP. SAED in S2 revealed single super-periodicity in <200> and <220> directions and double super-periodicity in <111> directions. Spacings in S2 (estimated error 1%) and the assigned crystal planes are shown in Table 1. In S3 only the fluorite phase was detected. Micrographs of S4 showed a material with a large unit cell related to the fluorite and pyrochlore (Fig. 2). The lattice spacings in S4 (SAED and DDP data) were multiples of the spacings in the fluorite phase; also faint spots were seen in SAED.

Super-periodicity in S2 was attributed to composition modulations due to ordering of defects. The lattice spacings indicated a double-cell with pyrochlore type structure. No evidence of a phase $Zr_3Y_4O_{12}$ with rhombohedral lattice [2] was obtained in the present HRTEM study. This is in agreement with TEM results in the literature [3]. Work is in progress to develop a structural model and reconcile the HRTEM data from S4 with the structure assigned from XRD powder data.

A correlation between thermal history (annealing, aging) and electrical conductivity in $(1-x)(ZrO_2)–x(Y_2O_3)$, with dominant fluorite phase, has been widely reported [1]. This effect has been attributed, at least in part, to order/disorder transitions. In this work domains with super-periodicity, within the fluorite phase, were imaged with atomic resolution. The presence of these domains depended on the annealing temperature. Coherency and average size of the domains will be investigated. The results of this work are of importance in interpreting changes of electrical conductivity with thermal history, in regimes of purely ionic conduction and of mixed conduction.

References

1. A, Brune, M. Lajavardi, D. Fisler and J.B. Wagner, Jr., *Solid State Ionics*, **106**, 89 (1998), and references therein.
2. V.S. Stubican, R.C. Hink and S. P. Ray, *J. Amer. Ceram. Soc.*, **61**, 17 (1978).
3. S. Suzuki, M. Tanaka and M. Ishigame, *Jap. J. Appl Phys.*, **24**, 401 (1985).

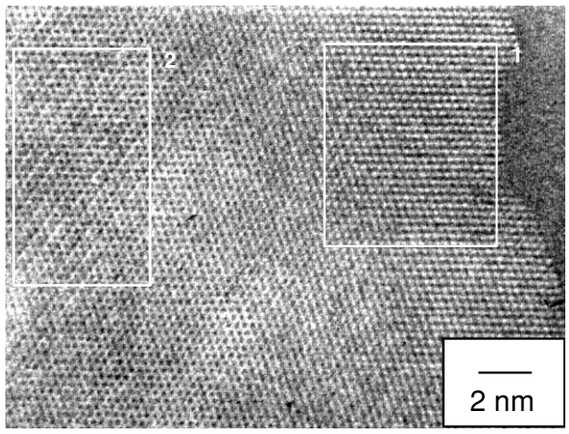

Fig. 1 HRTEM micrograph of sample S2 with 1: fluorite phase and 2: ordered domain.

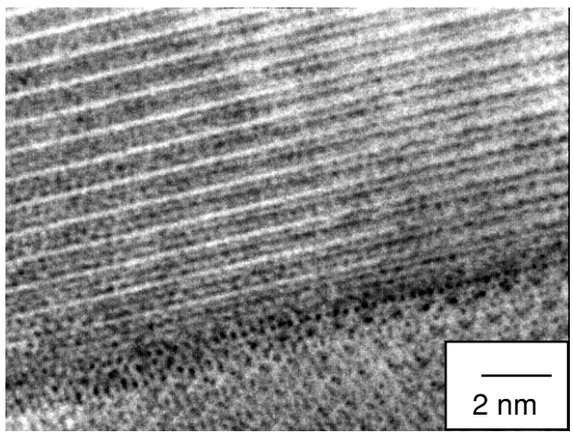

Fig. 2 HRTEM micrograph of sample S4.

sample S2 lattice spacings	(*)JCPDS-ICDD #30-1468
2.98: assigned (111)	2.968 (111)
2.59: " (200)	2.571 (200)
1.83: " (220)	1.818 (220)
5.95: " 2 x (111)	
5.15: " 2 x (200)	
3.62: " 2 x (220)	

Table 1. Lattice spacings of sample S2, evaluated from SAED and DDP, and the corresponding assigned (hkl) planes, based on (*) JCPDS powder diffraction data for 92 mol.% ZrO_2–8 mol.% Y_2O_3. All spacings are given in Angstroms. Electron beam direction: [011].